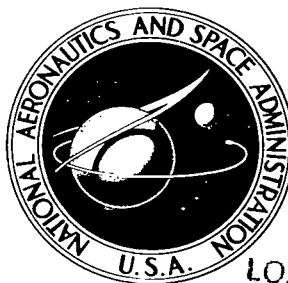


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ANALYTIC SOLUTIONS TO THE IGNITION KINETICS OF THE HYDROGEN-OXYGEN REACTION

by Richard S. Brokaw

*Lewis Research Center
Cleveland, Ohio*



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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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ANALYTIC SOLUTIONS TO THE IGNITION KINETICS

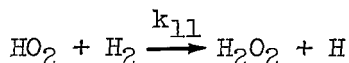
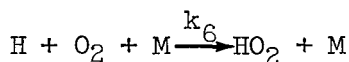
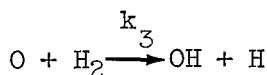
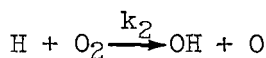
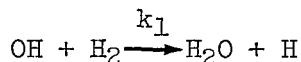
OF THE HYDROGEN-OXYGEN REACTION*

by Richard S. Brokaw

Lewis Research Center

SUMMARY

Solutions have been obtained by assuming isothermal conditions and negligible depletion of reactants during the induction period for the following scheme of reactions:



Three types of solutions have been deduced corresponding to $k_6 c_M > 2k_2$ (a low-temperature - high-pressure region of long ignition delays), $2k_2 > k_6 c_M$ (a high-temperature - low-pressure region of short delays), and $2k_2 = k_6 c_M$ (the boundary between the two regions). Experimental ignition delays in both long- and short-delay regions are adequately explained, and ignition delays computed by numerical integration of the rate equations are reproduced to within a few percent. Finally, ignition delays for the Von Neumann spike condition in Chapman-Jouguet detonations in the neighborhood of the lean limit of detonability in air have been calculated. These delays decrease by two orders of magnitude as the hydrogen mole fraction increases from 0.135 to 0.145. This is very close to the experimental limit (hydrogen mole fraction, 0.14 to 0.15) and thus supports the notion that the condition $2k_2 > k_6 c_M$ must be satisfied for a stable detonation.

INTRODUCTION

When hydrogen and air are instantaneously mixed at high temperature (as in

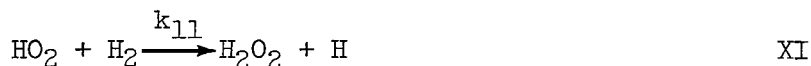
*This report was also presented as a paper at the Tenth International Symposium on Combustion, Cambridge, London, August 17 to 21, 1964.

idealized analyses pertinent to hypersonic ramjets, refs. 1 and 2), or when a mixture containing hydrogen and oxygen is subjected to a pulse of high temperature and pressure (as in shock tube ignition studies, refs. 3 and 4), the following events ensue: First, there is a very short period during which small concentrations of atoms and radicals - H, OH, and O - are produced. The mechanism of this initiation is uncertain and may vary under different circumstances. There follows the bulk of the induction period, during which the chain reaction is propagated and branched through the elementary reactions



The first reaction is not strongly exothermic (i.e., heat of reaction, 15 kcal/mole at 1000° K), while the second and third reactions are endothermic by 16 and 2 kilocalories, respectively. Thus, during most of the induction period, the atom and radical concentrations increase exponentially under essentially isothermal conditions. Very late in the induction period atom and radical concentrations become so large that self-heating occurs, which is largely due to the highly exothermic three-body recombination processes. The temperature rises precipitously, and the induction period is at an end.

At the lower temperatures and higher pressures the further reactions



must be considered as well. These five reactions, together with terms describing the destruction of chain carriers after diffusion to the walls, suffice to explain qualitatively the ignition behavior of the hydrogen-oxygen system, including the existence of the first, second, and third explosion limits.

The differential equations describing the chemical kinetics of reactions I, II, and III have been integrated numerically for hypersonic ramjet (refs. 1 and 2) and shock-tube (ref. 4) conditions. This report presents explicit analytic solutions that are excellent approximations to the numerical results; furthermore, reactions VI and XI have been included. Similar analytic solutions for reactions I to III and VI have been obtained by Kondratiev (ref. 5); Asaba, Gardiner, and Stubbeman (ref. 6) used the solution for reactions I to III to analyze results of their shock-tube experiments. The explicit analytic solutions developed in this report are valuable in that they permit one to determine easily the effects of variations in specific rate constants, temperature, pressure, initiation mechanism, etc., on ignition delays and the like. Some illustrative applications are presented and discussed.

THEORETICAL CONSIDERATIONS

The differential equations governing the growth of radical concentrations during the induction period are as follows:

$$\frac{dc_{OH}}{dt} = -k_1 c_{H_2} c_{OH} + k_2 c_{O_2} c_H + k_3 c_{H_2} c_O + i_{OH} \quad (1)$$

$$\frac{dc_H}{dt} = k_1 c_{H_2} c_{OH} - k_2 c_{O_2} c_H + k_3 c_{H_2} c_O - k_6 c_{O_2} c_M c_H + k_{11} c_{H_2} c_{HO_2} + i_H \quad (2)$$

$$\frac{dc_O}{dt} = k_2 c_{O_2} c_H - k_3 c_{H_2} c_O + i_O \quad (3)$$

$$\frac{dc_{HO_2}}{dt} = k_6 c_{O_2} c_M c_H - k_{11} c_{H_2} c_{HO_2} + i_{HO_2} \quad (4)$$

Here, the k 's are the specific reaction rate constants, the c 's are concentrations, and the i 's are rates at which the radicals are generated spontaneously, either in the gas phase or on the surfaces. (It is also possible to include destruction of radicals at the walls by including terms like $\gamma_w c_{OH}$, etc., in eqs. (1) to (4) with the coefficient γ_w , a function of diffusivity, pressure, geometry, and surface activity.)

During most of the induction period the kinetics of the elementary reactions I to III, VI, and XI can be represented as pseudo-first-order reactions; that is, they are all first order in the atom and radical concentrations - the only concentrations that are changing appreciably.

The initiation rates i_{OH} , etc., which are zero order in the radical concentrations, can be eliminated from equations (1) to (4) by means of the substitutions (ref. 7)

$$c'_{OH} \equiv c_{OH} + \frac{i_H + i_O + i_{HO_2}}{k_1 c_{H_2}} \quad (5)$$

$$c'_H \equiv c_H + \frac{i_{OH} + i_H + 2i_O + i_{HO_2}}{2k_2 c_{O_2}} \quad (6)$$

$$c'_O \equiv c_O + \frac{i_{OH} + i_H + i_{HO_2}}{2k_3 c_{H_2}} \quad (7)$$

$$c'_{HO_2} \equiv c_{HO_2} + \frac{k_6 c_M}{2k_2 k_{11} c_{H_2}} \left[i_{OH} + i_H + 2i_O + \left(1 - \frac{2k_2}{k_6 c_M} \right) i_{HO_2} \right] \quad (8)$$

These initiation rates are presumably very small compared with the rates of reactions I to III, so that the correction terms of equations (5) to (8) are

negligible except in the very initial portion of the induction period. Consequently, in what follows these corrections will be neglected. They should be considered, however, in any detailed analysis of the kinetics of initiation. Inclusion of these terms poses no mathematical problem; they simply increase algebraic complexity.

The system of differential equations (eqs. (1) to (4)) may be solved by the method outlined by Frost and Pearson (ref. 8) if it is assumed that the concentrations of reactants - H_2 , O_2 and M - are constant and neglecting i_{OH} , i_H , i_O , and i_{HO_2} (or applying eqs. (5) to (8)). A set of particular solutions is

$$c_i = A_i e^{\lambda t} \quad i = OH, H, O, HO_2 \quad (9)$$

where A_i is a constant with dimensions of concentration and λ is a constant with dimensions of reciprocal time. Substituting equations (9) into equations (1) to (4) yields the relations

$$-(k_1 c_{H_2} + \lambda) A_{OH} + k_2 c_{O_2} A_H + k_3 c_{H_2} A_O = 0 \quad (10)$$

$$k_1 c_{H_2} A_{OH} - (k_2 c_{O_2} + k_6 c_{O_2} c_M + \lambda) A_H + k_3 c_{H_2} A_O + k_{11} c_{H_2} A_{HO_2} = 0 \quad (11)$$

$$k_2 c_{O_2} A_H - (k_3 c_{H_2} + \lambda) A_O = 0 \quad (12)$$

$$k_6 c_{O_2} c_M A_H - (k_{11} c_{H_2} + \lambda) A_{HO_2} = 0 \quad (13)$$

A nontrivial solution requires that the determinant of the coefficients of the A_i be zero (ref. 8). This leads to the quartic equation

$$\begin{aligned} \lambda^4 + & \left[(k_1 + k_3 + k_{11}) c_{H_2} + (k_2 + k_6 c_M) c_{O_2} \right] \lambda^3 \\ & + \left[k_1 k_3 c_{H_2}^2 + (k_1 + k_3) k_6 c_{H_2} c_{O_2} c_M + (k_1 c_{H_2} + k_2 c_{O_2} + k_3 c_{H_2}) k_{11} c_{H_2} \right] \lambda^2 \\ & + k_1 k_3 c_{H_2}^2 \left[(k_6 c_M - 2k_2) c_{O_2} + k_{11} c_{H_2} \right] \lambda - 2k_1 k_2 k_3 k_{11} c_{H_2}^3 c_{O_2} = 0 \end{aligned} \quad (14)$$

From Decartes' rule of signs, it is found that this equation has one positive root, one negative root, and two roots that are either negative or conjugate complex. The positive root is desired since it governs the exponential growth of radical concentrations during the induction period. The other roots are important only in the initiation phases of the reaction - their effect on the radical concentrations dies out (more or less quickly depending on their absolute magnitude). The rate constant k_{11} is very small in comparison with k_1 , k_2 , k_3 , and $k_6 c_M$. Therefore the additive terms involving k_{11} in the coefficients of λ , λ^2 , and λ^3 may be neglected.

Approximations to the positive root of equation (14) will be derived for three conditions: $k_6 c_M > 2k_2$, $k_6 c_M = 2k_2$, and $k_6 c_M < 2k_2$.

$k_6 c_M > 2k_2$. - This regime corresponds to the conditions above the third explosion limit. This is a region of long ignition lags, with delays of several seconds at 560° to 600° C and atmospheric pressure. Correspondingly, the positive λ is very small, and it is found that λ^2 , λ^3 , and λ^4 may be set equal to zero in equation (14). The result is

$$\lambda \cong \frac{2k_2 k_{11} c_{H_2}}{k_6 c_M - 2k_2} \quad (15)$$

This expression is a very good approximation indeed, except very close to the second limit condition, where the denominator approaches zero. Note that at high pressure $\lambda \rightarrow 2k_2 k_{11} c_{H_2} / k_6 c_M$, which is independent of pressure.

$k_6 c_M = 2k_2$ (Second limit condition). - Above the junction of the second and third limits this condition marks the boundary between regions of long and short ignition delay. Here the coefficient of λ in equation (14) is zero (neglecting the term in k_{11}). Again, λ^3 and λ^4 may be neglected; the result is

$$\lambda \cong \left[\frac{2k_1 k_2 k_3 k_{11} c_{H_2}^2 c_{O_2}}{k_1 k_3 c_{H_2} + (k_1 + k_3) k_6 c_{O_2} c_M} \right]^{1/2} \quad (16)$$

$2k_2 > k_6 c_M$. - This corresponds to the important region of short ignition delays at high temperatures and modest pressures. Under these conditions the coefficient of λ in equation (14) reduces to the cubic equation

$$\lambda = \frac{k_1 k_3 (2k_2 - k_6 c_M) c_{H_2}^2 c_{O_2}}{k_1 k_3 c_{H_2}^2 + (k_1 + k_3) k_6 c_{H_2} c_{O_2} c_M + [(k_1 + k_3) c_{H_2} + (k_2 + k_6 c_M) c_{O_2}] \lambda + \lambda^2} \quad (17)$$

which was first derived by Kondratiev (ref. 5). Note that, if λ is small, the terms involving λ and λ^2 in the denominator are unimportant. If, in addition, k_1 , k_2 , and k_3 are much larger than $k_6 c_M$, λ approaches $2k_2 c_{O_2}$. This provides the basis of the ignition delay correlation used by Scott and Kinsey (ref. 3).

Equation (17) has a further interesting aspect. Suppose one has an approximate value of λ , designated λ_1 . The right side of equation (17) can thus be used to generate a second approximation, λ_2 . A positive root is needed. Hence, if λ_1 is too small, λ_2 is too large; if λ_1 is too large, λ_2 is too small. Thus, the correct solution is bracketed, and the approximation $\lambda \cong (\lambda_1 \lambda_2)^{1/2}$ should be in error by less than half the error of the worst of the two estimates.¹

¹Note that, if the error in λ_2 is less than twice the error in λ_1 , the geometric mean value (call it λ_3) is clearly superior to λ_1 . Thus, λ_3 can be substituted into eq. (17) to obtain an improved approximation, λ_4 ; and $\lambda_5 \equiv (\lambda_3 \lambda_4)^{1/2}$ will be an improvement over $\lambda_3 \equiv (\lambda_1 \lambda_2)^{1/2}$. This provides an iterative procedure that will converge on the true value of λ .

An approximate solution can be obtained by invoking the steady-state approximation in OH (by setting eq. (1) equal to zero). Thus, equation (1) can be used to eliminate the OH concentration from equations (2) and (3), which can then be solved with the result

$$\lambda_1 = \frac{k_3 c_{H_2} + k_6 c_{O_2} c_M}{2} \left\{ \left[1 + \frac{4k_3(2k_2 - k_6 c_M) c_{H_2} c_{O_2}}{(k_3 c_{H_2} + k_6 c_{O_2} c_M)^2} \right]^{1/2} - 1 \right\} \quad (18)$$

This result, in turn, may be substituted into equation (17) to obtain λ_2 , so that the final approximation to λ is

$$\lambda \cong (\lambda_1 \lambda_2)^{1/2}$$

$$= \left(\frac{k_1 k_3 (2k_2 - k_6 c_M) c_{H_2}^2 c_{O_2} \left\{ \left[1 + \frac{4k_3(2k_2 - k_6 c_M) c_{H_2} c_{O_2}}{(k_3 c_{H_2} + k_6 c_{O_2} c_M)^2} \right]^{1/2} - 1 \right\}}{2k_2 c_{O_2} \frac{k_3 c_{H_2} - k_6 c_{O_2} c_M}{k_3 c_{H_2} + k_6 c_{O_2} c_M} + (k_1 c_{H_2} + k_2 c_{O_2}) \left\{ \left[1 + \frac{4k_3(2k_2 - k_6 c_M) c_{H_2} c_{O_2}}{(k_3 c_{H_2} + k_6 c_{O_2} c_M)^2} \right]^{1/2} + 1 \right\}} \right)^{1/2} \quad (19)$$

It is possible, of course, to obtain other first approximations λ_1 by assuming steady states in H or O rather than in OH. The following table shows some numerical comparisons with these other techniques calculated for a mixture of 5 percent hydrogen in air; the rate constants are from reference 4, and k_6 has been set equal to zero. The assumption of a steady state in OH gives clearly superior values of λ_1 , although the final approximations $(\lambda_1 \lambda_2)^{1/2}$ are remarkably good in all cases. The OH concentration is smallest, so it seems reasonable that the steady-state approximation should apply best to this radical. (The true values of λ were obtained by numerical solution of eq. (17).)

Steady state in -	λ , sec ⁻¹	Temperature, °K	
		1100	1900
		Pressure, atm	
		0.2307	0.4873
OH	λ_1	2.67×10^4	3.70×10^5
	λ_2	2.39	2.02
	$(\lambda_1 \lambda_2)^{1/2}$	2.526	2.734
H	λ_1	10.1×10^4	4.58×10^5
	λ_2	.685	1.616
	$(\lambda_1 \lambda_2)^{1/2}$	2.630	2.720
O	λ_1	8.76×10^4	16.8×10^5
	λ_2	.793	.360
	$(\lambda_1 \lambda_2)^{1/2}$	2.638	2.460
	True value	2.503×10^4	2.727×10^5

Once the value of λ has been obtained, relations among A_{OH} , A_H , A_O , and A_{HO_2} follow from equations (10) to (13).

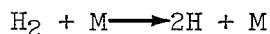
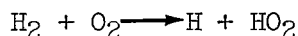
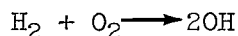
It remains merely to discuss the boundary conditions defining the beginning and the end of the ignition delay period. For simplicity it will be assumed that the initiation phase

of the induction period is very short and may be neglected in comparison with the total span of the delay before ignition. (As indicated heretofore, it is possible to obtain analytic solutions without this assumption, but at the expense of algebraic complexity. Further a detailed knowledge of the initiation kinetics would be required.)

Assume that the initiation process produces radicals by some bimolecular process:

$$i_1 = \left(\frac{dc_1}{dt} \right)_{t=0} \propto c_M^2 \quad (20)$$

where c_M represents the total concentration of stable species. Examples of reactions of this sort could include



and others as well. It is reasonable to assume that, initially, the rate of formation of radicals is equal to the rate of consumption in reactions such as I, II, III, etc., (which are first order in the radical, but second order overall):

$$\left(\frac{dc_1}{dt} \right)_{t=0} \propto c_M A_1 \quad (21)$$

where A_1 is an effective initial radical concentration (see eq. (9)). Thus, in general, from equations (20) and (21),

$$A_1 = \text{const } c_M = a_1 p \quad (22)$$

where p is pressure and a_1 is an appropriate constant of proportionality. Hence, the radical concentration as a function of time is

$$c_1 = a_1 p e^{\lambda t} \quad (23)$$

as long as initiation is in the gas phase and requires only a small fraction of ignition delay.

The end of the induction period can be defined in a number of ways that are qualitatively equivalent. For example, Schott and Kinsey (ref. 3) define the end of the delay period as the time at which the concentration of some species reaches a characteristic level (in their case, $c_{OH} = 10^{-6}$ mole/liter). Thus, from equation (23),

$$\lambda \tau = B - \ln p \quad (24)$$

where τ is the ignition delay and B is a constant. The same result is obtained if one characterizes the end of the delay period by a critical rate of temperature rise due to three-body radical recombination

$$c_M c_p \left(\frac{dT}{dt} \right)_{\text{crit}} \propto c_i c_j c_M \Delta H_{ij} \propto c_M p^2 e^{2\lambda \tau} \quad (25)$$

which again leads to equation (24). Again, if one assumes a critical rate of temperature rise due to a bimolecular process such as reaction I, equation (24) follows once more. Thus, a variety of reasonable assumptions about the initiation and the termination of the induction period all lead to expressions of the form of equation (24).

ILLUSTRATIVE APPLICATIONS

In this section, the foregoing theoretical results are applied to calculate ignition delays for hydrogen-air systems under a variety of conditions of practical interest, including (1) the low-temperature region of moderate pressures, where ignition delays of one to several seconds are observed, (2) the higher-temperature low-to-moderate-pressure regime, where delays range from several microseconds to several milliseconds, and finally (3) the high-temperature - high-pressure boundary between these regimes, which seems to be of importance in determining limits of detonability.

Region of Long Delays

Ignition delays for hydrogen in air were measured some three decades ago by Dixon (ref. 9), who used an apparatus in which a heated stream of hydrogen was injected into a larger concentric stream of heated air. Interpolated delays at 600° C are shown in figure 1.

In this regime, the characteristic parameter λ (used in eq. (24) to compute the ignition delay τ) is given by equation (15). From figure 1 it is clear that, at a pressure close to 1/2 atmosphere, the ignition delays become very short, as k_6 approaches $2k_2$. This provides a key for determining the effective hydrogen concentration (which is otherwise indeterminate in Dixon's experiment), because k_6 is a function of the nature of the third body, M. It is assumed here that

$$k_6 = 3.27 \times 10^{15} (x_{H_2} + 0.35 x_{O_2} + 0.43 x_{N_2} + 0.2 x_{Ar} + 14.3 x_{H_2O} + \dots) T^{-1.92} \quad \text{liters}^2/(\text{mole})^2(\text{sec}) \quad (26)$$

where the x 's are the mole fractions of various third bodies. Equation (26) is consistent with Clyne's room temperature measurement, with argon as a third body (ref. 10), and Baldwin's estimates at 540° C (ref. 10). The relative third-body efficiencies are taken from reference 11. Using k_6 from equation (26) and k_2 from reference 4 gives an effective mole fraction of hydrogen of 0.22. This procedure may seem somewhat arbitrary, but it is comforting that the hydrogen mole fraction did not turn out to be negative (limit pressure > 0.66 atm) or greater than unity (limit pressure < 0.27 atm)!

The curve in figure 1, computed by assuming $k_{11} = 5.2 \times 10^2$ liters per mole per second and $B = 3.8$, provides a very good fit of the experimental data. This value of k_{11} is greater than that suggested by Voevodsky (ref. 12) by a factor of 4.5. The cause of this discrepancy is uncertain: Voevodsky perhaps deduced his k_{11} by assuming somewhat different values of k_2 and k_6 ; but on

the other hand our kinetic scheme is probably oversimplified. Furthermore, the effective hydrogen concentration may vary with pressure.

Other observations by Dixon (ref. 9) are also easily understood from these

theoretical relations. Thus, he reported ignition delays in oxygen slightly shorter than those in air. This is not surprising since the oxygen concentration does not appear explicitly in equation (15); its only effect is to cause a slight decrease in k_6 (see eq. (26)). On the other hand, Dixon (ref. 9) reported markedly longer delays in the presence of water vapor. This is due to the fact that water is a very efficient third body, so that k_6 is considerably increased.

The effect of hydrogen concentration on the ignition delay has been determined by Anagnostou, Brokaw, and Butler (ref. 13); some of their results near 600° C are shown in figure 2. (They found some variation according to the mode of operation of their apparatus; the shortest delays at this temperature were roughly half as large as those shown in

fig. 2.) The curve in figure 2 has been calculated from equations (15) and (24) with the same constants used to fit Dixon's data in figure 1. Thus, the experimental composition dependence is rather well predicted: $\tau \propto p_{H_2}^{-0.6}$.

It seems then that the analytic solutions presented in this report describe the behavior of the hydrogen-oxygen reaction in the region of long delays rather well.

Region of Short Delays

Ignition delays for hydrogen-air have been calculated numerically by Momtchiloff, Taback, and Buswell (ref. 1) and Belles and Lauver (ref. 4) with different assumptions as to the mechanism of initiation. Momtchiloff, Taback, and Buswell use Schott and Kinsey's criterion for ignition ($c_{OH} = 10^{-6}$ mole/liter,

ref. 3); Belles and Lauver (ref. 4) give constants for equation (9) so that Schott and Kinsey's criterion is easily applied to their calculations as well. (Both papers neglect reaction VI.)

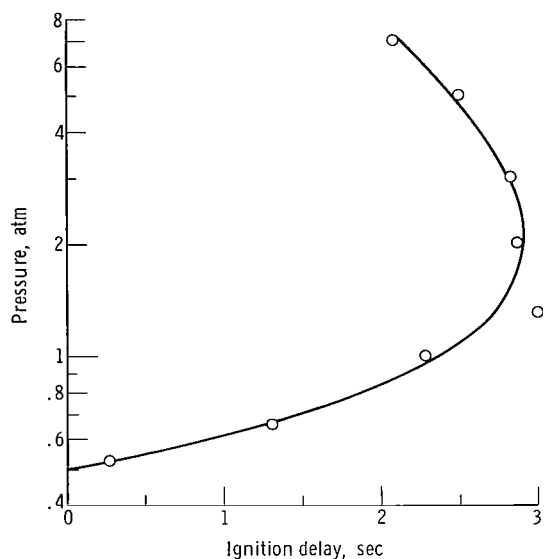


Figure 1. - Effect of pressure on hydrogen-air ignition delays at 600° C (ref. 9).

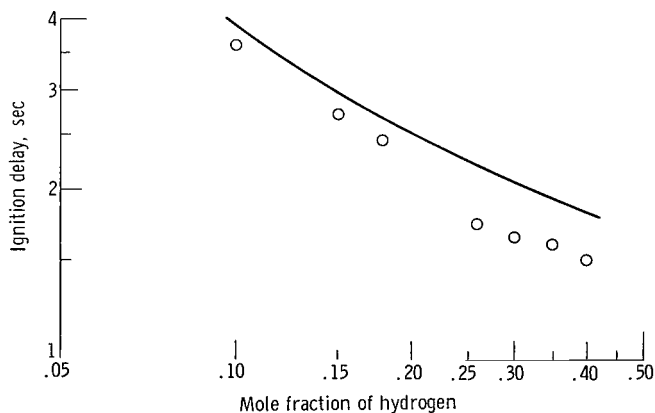


Figure 2. - Effect of hydrogen concentration on hydrogen-air ignition delays at 594° C and 1 atmosphere (ref. 13).

The analysis of reference 1, presumably pertinent to hypersonic ramjets, assumes equilibrium concentrations of hydrogen and oxygen atoms in the hydrogen and air streams prior to instantaneous mixing. The hydrogen atoms are expected to be more important because of their higher equilibrium concentration. Thus, the growth of OH radical concentration with time is

$$c_{OH} = c_{H,eq} \frac{A_{OH}}{A_H} e^{\lambda t} \quad (27)$$

Using equations (10) and (11), neglecting reactions VI and XI, gives

$$\frac{A_{OH}}{A_H} = \frac{2k_2 c_{O_2} + \lambda}{2k_1 c_{H_2} + \lambda} \quad (28)$$

Thus, the induction times computed numerically in reference 1 can be approximated from equations (19), (27), and (28). Numerical and approximate analytic results are compared in the following table.

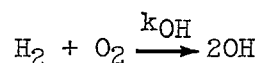
Temperature, °K	Pressure, atm	Mole fraction of hydrogen	Ignition delay, μsec	
			Approximate (a)	Numerical
973	1.0	0.296	240	^b 260
1667	1.0	.296	5.3	^b 5.1
1100	.2307	.05	866	^c 866
1900	.4873	.05	33.6	^c 32.6

^aThis report.

^bRef. 1.

^cRef. 4.

Belles and Lauver (ref. 4), on the other hand, assume initiation by the reaction



If it is assumed that, initially, the rate of production of OH radicals in this reaction equals the rate of their consumption in reaction I,

$$A_{OH} = \frac{2k_{OH}c_{O_2}}{k_1} \quad (29)$$

so that the ignition delay is

$$\lambda\tau = \ln \left(\frac{c_{OH,crit}}{A_{OH}} \right) = \ln \left(\frac{k_1 \times 10^{-6}}{2k_{OH}c_{O_2}} \right) \quad (30)$$

Numerical (ref. 4) and analytic results from equation (30) are compared in the previous table. It is clear that the analytic solutions are very good approximations to the numerical results, both for very lean and stoichiometric conditions, and for two rather different assumptions as to the initial source of radicals.

By studying stationary hydrogen-air flames in a flow system, Fouré (ref. 14) has obtained information on ignition delays in the region of short delays. Fouré heated flowing homogeneous fuel-air mixtures to a temperature somewhat below the point of spontaneous ignition. The mixture, traveling at a

high subsonic velocity, then passed through a diffuser into a reaction tube. The velocity decrease to about 40 meters per second was accompanied by increases in temperature and pressure that rendered the mixtures spontaneously inflammable. Temperature and composition profiles were obtained by probing the extended reaction zone formed some distance downstream of the diffuser. The distance from the diffuser exit to the point of appreciable temperature rise provides an indication of ignition delay times; however, the choice of the diffuser exit as a zero point is somewhat arbitrary since reaction may actually start within the diffuser. Fouré's results are shown in figure 3. A millisecond scale has been added based on the assumption that the velocity in the reaction tube was 40 meters per second.

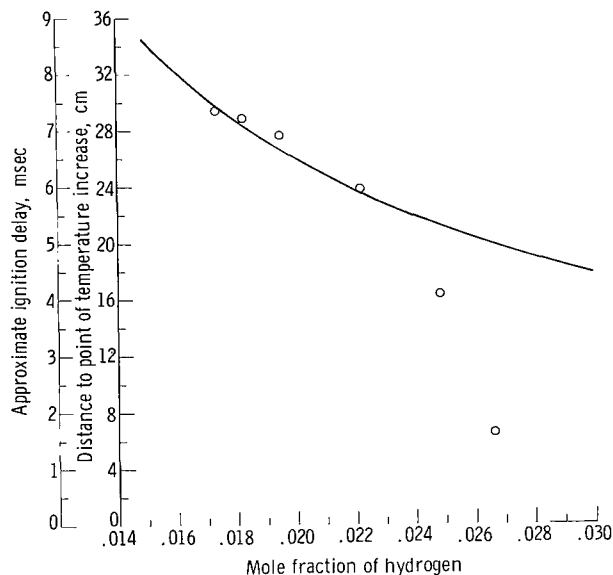


Figure 3. - Effect of hydrogen concentration on hydrogen-air ignition delays for $658 \pm 2^\circ\text{C}$ and 1 atmosphere (ref. 14).

Ignition delays computed from equations (19) and (24) are shown by the curve in figure 3. The constant B has been taken as 25 so as to fit the experimental data at the leaner compositions. (This agrees very well with eq. (30), which predicts $B = 25.6$ at 913°K .) The deviation of the two richest mole fractions suggests that there may have been considerable reaction in the diffuser under these conditions.

Fouré was unable to observe any temperature rise in his ignition tube below 910°K . Since the tube was 1 meter long and the flow velocity was about 40 meters per second, ignition delay must have been in excess of 25 milliseconds. If $B = 25$ is again assumed, an ignition delay of 54 milliseconds is computed. At this condition, the delay is extremely sensitive to the temperature. If the temperature is raised but 1 degree the delay decreases to 40 milliseconds, and hence a 25-millisecond delay would occur

at 912° or 913°K . Thus, the present analysis predicts Fouré's lower temperature limit within 3°K .

A further point merits some discussion. The ignition delays in the region of long delays were fit assuming $B \approx 3.8$ at 600°K , whereas the short delay data require $B \approx 25$ at a temperature some 60° higher. From equations (20) to (25), it appears that

$$B = - \ln \left(\frac{dc_i}{dt} \right)_{t=0} + 2 \ln p + \text{const}$$

so that a small value of B indicates a large initiation rate and vice versa. Thus, it appears that the initiation mechanisms in the long- and short-delay regions are distinctly different, and the long delay initiation rate is larger

by perhaps nine orders of magnitude (although this changes the delays by less than one order of magnitude). There is evidence (ref. 15) that hydrogen peroxide plays an important role in the initiation of the hydrogen-oxygen reaction in the neighborhood of the second limit. Hydrogen peroxide is produced in reaction XI, which is important principally in the long-delay regime.

Finally, it should be noted that this approximate solution for the region of short ignition delays adequately represents shock-tube ignition data on the hydrogen-oxygen system over a very wide range of mixture ratio (ref. 16).

Boundary Between Long- and Short-Delay Regions (and Limits of Detonability)

A stable detonation wave involves the coupling of a shock front with a rapid chemical heat release, which, in turn, sustains the shock. Thus, the heat release must occur rather close to the shock in a stable detonation.

Belles (ref. 17) has proposed that, in the case of the hydrogen-oxygen reaction, the limits of detonability may be predicted by requiring that in a stable detonation the second limit condition $2k_2 \geq k_{6CM}$ be satisfied in the Von Neumann spike accompanying the detonation front. (These conditions of temperature and pressure are calculable from the Chapman-Jouguet detonation Mach number, and the adiabatic shock relations for the nonreacting gas at the same Mach number.) Using the second limit criterion, Belles predicted lean and rich limits of detonability for hydrogen-oxygen and hydrogen-air in good agreement with experiment.

Belles applied the second limit criterion under conditions of temperature ($\sim 1300^\circ \text{K}$) and pressure ($\sim 20 \text{ atm}$) where hydrogen-oxygen and hydrogen-air mixtures invariably ignite spontaneously (in other words, at temperatures above the junction of the second and third explosion limits). Thus, he tacitly assumes that there is a "memory" of the second limit - a demarcation between regions of long and short delay.

To examine this notion further, ignition delays have been calculated for conditions around the lean limit of detonability for hydrogen-air mixtures. Chapman-Jouguet Mach numbers were computed as described by Zeleznik and Gordon (ref. 18), and then conditions immediately behind the shock were deduced by using ideal shock relations for a gas of $\gamma = 1.4$ (ref. 19). For initial conditions of room temperature and atmospheric pressure with hydrogen concentrations of 12 to 16 percent in air, the Von Neumann spike pressures and temperatures are in the ranges 16 to 20 atmospheres and 1100° to 1300°K , respectively. Delays have been computed from equation (30) with rate constants for the initiation reaction and reactions I, II, and III from reference 4. Rate constants for reaction VI were obtained from equation (26) and the constants for reaction XI were taken as

$$k_{11} = 5.4 \times 10^8 \exp\left(\frac{-24,000}{RT}\right) \quad \text{liters}/(\text{mole})(\text{sec})$$

which is simply 4.5 times the value suggested by Voevodsky (ref. 12).

Results are shown in figure 4. Clearly there is an abrupt decrease in ignition lag around a hydrogen mole fraction of 0.14; the ignition delay decreases by two orders of magnitude as the hydrogen concentration is increased 0.01. This provides further support to Belles' postulate that the condition $2k_2 \geq k_6 C_M$ must be satisfied for stable detonations in the hydrogen-oxygen system.

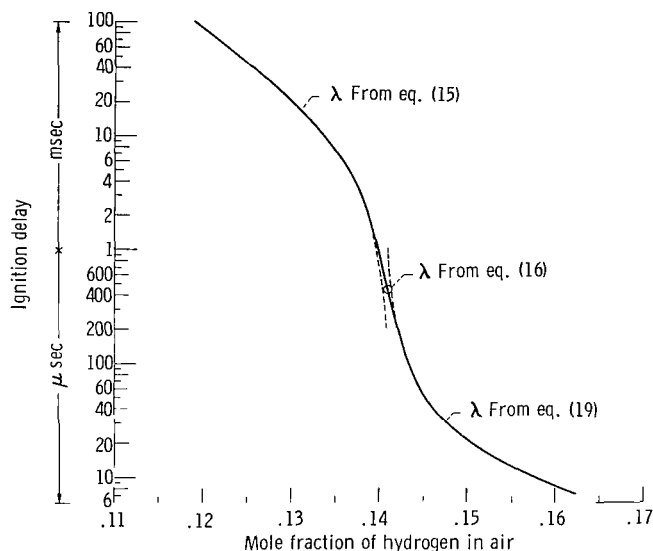


Figure 4. - Ignition delays for Von Neumann spike condition in Chapman-Jouguet detonation of hydrogen-air in neighborhood of lean limit of detonability.

Experimentally, the lean limit of detonability of hydrogen-air mixtures lies in the range 14 to 15 percent hydrogen by volume (ref. 20).

CONCLUDING REMARKS

It is hoped that the examples discussed in the preceding section illustrate the usefulness of these analytic solutions as applied to a variety of problems. Further analysis of this sort may help uncover more detailed information on the hydrogen-oxygen reaction. Some other applications suggest themselves:

(1) The concentrations of labile intermediates - H, OH, O, HO₂, etc. - can be computed as a function of time throughout the induction period. Thus, one can explore the feasibility of detecting these species experimentally, for instance, spectroscopically, or with electron paramagnetic resonance techniques, or the mass spectrometer.

(2) By analyzing experimental ignition delay data obtained under a variety of conditions, it should be possible to glean information as to the mechanism of initiation, that is, the process by which atoms and free radicals are first generated from the reactants (by analysis of the term B in eq. (24)).

(3) By computing delays near the low-pressure limits of detonability, it may be possible to gain insight as to the degree of coupling between shock front and reaction zone required in a stable detonation.

(4) If need be, other chemical reactions may be added to the scheme. (This may be desirable particularly in the high-pressure - low-temperature region.) There is a restriction, however. Reactions must be first order in the intermediates or products. Thus, reactions such as $H + H_2O_2 \rightarrow H_2O + OH$ cannot be considered.

(5) Finally, the general method of attack used here should be useful in obtaining solutions to the kinetics for other isothermal branched chain explosions.

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National Aeronautics and Space Administration
Cleveland, Ohio, March 26, 1964

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